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<p>(54) Title: <b>HEAT TREATED NONCOHESIVE STARCHES AND FLOURS AND PROCESS FOR THEIR PRODUCTION</b></p> <p>(57) Abstract</p> <p>A process for making a heat treated, non-chemically modified, noncohesive starch or flour comprises the steps of providing a native, granular starch of a flour at a neutral or basic pH, dehydrating it to a moisture content of preferably less than 5 % by weight, and heating the starch or flour at greater than 100 °C for a period of time effective to obtain a product that is noncohesive when dispersed in an aqueous medium and gelatinized. The starch of flour is used in place of chemically cross-linked starches or flours.</p>		

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## HEAT TREATED NONCOHESIVE STARCHES AND FLOURS AND PROCESS FOR THEIR PRODUCTION

5           This invention relates to a method for making noncohesive starch or flour (hereinafter "starch") from a native granular starch at a neutral or basic pH, dehydrated to a moisture content preferably less than 5%, and then heated with sufficient dry heat for a time and at a temperature effective to produce a starch inhibited from breakdown in  
10   viscosity and with noncohesive properties after gelatinization. The starch may be used in place of chemically modified or crosslinked starches presently used in foods, and in other applications, such as in the manufacture of paper and packaging.

          The processed foods industry has sought to satisfy consumer  
15   demands for foods containing starches that have not been chemically modified but that have the same physical and functional properties as chemically modified starches. For example, starches are chemically modified with reagents, such as phosphorus oxychloride, sodium tri-meta-phosphate, adipic and acetic anhydrides and epichlorohydrin, to  
20   produce chemically crosslinked starches having excellent tolerance to processing variables such as heat, shear and extremes of pH. Such chemically crosslinked starches provide a desirable smooth texture to the processed food product and maintain their capacity for thickening throughout processing operations and storage of the food during

normal shelf life. In contrast, unmodified starches are characterized by a breakdown in viscosity, loss of thickening capacity and textural qualities, and exhibit unpredictable behavior during shelf life as a result of the stresses applied during food processing. These stresses tend to fully disrupt the starch granule and disperse it into the food, permitting the starch molecules to be hydrolyzed by heat, shear and extreme pHs, particularly acidic pHs, making the unmodified starches unsuitable for use in processed foods.

The process of this invention is a heat treatment process that accomplishes the purposes of chemical modification of starches without use of typical chemical reagents. It also permits the food manufacturer to avoid label declarations associated with the chemical modification of starch, and, thereby, provide a perceived consumer benefit.

Heat treatment of waxy maize starch at naturally occurring pH to remove woody flavors and modify texture on pregelatinization is disclosed in U.S. Patent number 4,303,451, issued December 1, 1981, to Seidel, et al. The starch is heated with dry heat at a temperature within the range of 120° to 200°C to give consistently acceptable nonwoody flavor and improved texture in the pregelatinized starch.

Heat treatment of waxy corn starch and waxy corn starch derivatives to provide a starch with emulsification properties to replace

gum arabic is disclosed in Japanese Patent Publication No. 61-254602, published December 11, 1986. In this process, the starch is heated preferably under acidic conditions of pH 4.0-5.0 to hydrolyze the starch to obtain emulsification properties. The heating step is  
5 carried out at a temperature from 100° to 200°C with the optimum temperature being 130° to 150°C for 0.5 to 6 hours.

Smoke treatment of waxy corn starch to improve gel strength is disclosed in U.S. Patent number 4,303,452. In order to counteract the acidity of the smoke and to obtain a final starch product with a pH of  
10 4 to 7, the pH of the starch is raised to a range of 9-11 before smoking. The preferred water content of the starch during the smoking is 10-20%.

There remains a need for starches that have noncohesive characteristics and that resemble chemically modified or crosslinked  
15 starches, that is, are stable to heat, pH and shear forces encountered in various industrial and food processing operations, such as, paper and corrugated paper board manufacturing, and retorting or pasteurizing canned or jarred foods. In particular, there is a need for a starch that does not contribute a cohesive character to processed  
20 food. It has now been discovered that such a starch may be prepared by the method of this invention.

### Summary of the Invention

This invention is a process for making a starch treated with heat that is the functional equivalent to a chemically crosslinked or modified starch. Initially, it should be noted that when certain native starches (particularly waxy based starches) are gelatinized, they reach a peak viscosity, which soon begins to break down as that the starch polymers dissociate and become solubilized, thereby causing the starch paste to become cohesive or runny. In contrast, when the starches made according to this process are dispersed in an aqueous medium and gelatinized, the starches have a viscosity more inhibited to breakdown relative to starches that are not heat treated according to this process. The inhibition to breakdown correlates to what is subjectively a noncohesive, or "short" texture, meaning the gelatinized starch tends to be salve-like and heavy in viscosity rather than runny or gummy.

The process comprises the steps: a) providing a native granular starch at neutral or basic pH; b) dehydrating the starch to a moisture content of 5% or less; and c) heating the dehydrated starch at a temperature of 100°C or greater for a period of time effective to cause the starch to be noncohesive when it is dispersed in an aqueous medium and gelatinized, the heat treated starch being the functional equivalent to a chemically crosslinked or modified starch.

As used herein, "native" means a starch that has not been chemically crosslinked, modified, or treated in any way, and "heat treated starch" means a starch at neutral to basic pH heated with sufficient dry heat to provide a starch having functional characteristics similar to those of a chemically crosslinked or modified starch.

The peak viscosity and viscosity breakdown of the heat treated starches after gelatinization will vary depending on the processing conditions (initial pH of the starch, moisture content of the starch during heating, heating temperature and time), and can vary over a broad range. Although the peak viscosity generally is lower than the peak viscosity of the same non-heat treated native starch, the viscosity will be stable, i.e. inhibited from breakdown. Breakdown, for purposes herein, is measured as the difference between the peak viscosity and the viscosity at a specific time (usually 10 or 20 minutes) after peak viscosity under specific conditions when measured on a Brabender Viscoamylograph. For example, the peak viscosity of a heat treated waxy maize starch can be as high or greater than 600 Brabender Units with a breakdown of less than 100 Brabender units, measured at pH 3, 5.0% starch solids, and heated to 92°C. In this case, a breakdown in starch viscosity of less than about 100 Brabender units correlates to a starch with a short, noncohesive texture, similar to the texture imparted by chemical crosslinking or modification. (Such starches,

whether heat treated by the process of this invention or chemically treated, are termed inhibited.)

The preferred starting starches are native granular waxy maize, low temperature stable waxy maize hybrid ("V.O. hybrid"), waxy rice, waxy barley, tapioca, and potato. The process may be carried out as part of a continuous process including the extraction of the starch from a plant material. This invention also provides starches and flours prepared by the process herein, as well as food products comprising at least one starch or flour prepared by the method of this invention.

10 The starches and flours useful in the process of this invention may be derived from any native source, including corn, pea, potato, sweet potato, barley, wheat, rice, sago, amaranth, tapioca, sorghum, waxy maize, waxy rice, waxy barley and the like. A suitable starch is described in U.S. Patent number 4,428,972, issued January 31, 1984, 15 to Wurzburg, et al. Unless specifically distinguished, all references to starches herein include their corresponding flours. The conversion products derived from any of these native starches, including fluidity or thin-boiling starches prepared by oxidation, alpha-amylase conversion, mild acid hydrolysis or heat dextrinization, may be used.

20 The converted starches may be prepared by any one of several methods that are well known in the art. See, e.g., M. W. Rutenberg, "Starch and Its Modifications" pages 22-36, *Handbook of Water-*



*Soluble Gums and Resins*, R. L. Davidson, Editor, McGraw-Hill, Inc., New York, NY, 1980. Enzyme conversion of the starch may be carried out by the method disclosed in U.S. Patent No. 4,726,957 to Lacourse, et al. A combination of conversion techniques may be used. The  
5 conversion is typically carried out before the process of this invention, but may be carried out afterwards. The converted base starch would not be suitable for use in applications where a high viscosity starch is required.

While other starch modifications may be carried out on a  
10 granular native starch prior to the process of this invention, these modifications (e.g., ether and ester derivatization) are not desired in applications where a food manufacturer requires a nonchemically modified product.

Providing a starch at a pH of neutral or above before the  
15 dehydration and heating steps is believed to reduce or eliminate the potential for any acid hydrolysis of the starch that may occur during those steps. Therefore, adjustment of the pH is preferably done before the dehydration step. However, if the dehydration conditions are not severe, pH adjustment may be done after the dehydration step, or both  
20 before and after.

Native granular starches typically have a pH of about 5.0 to 6.5. If the pH of the starch is naturally in the range of neutral or above, the

starch may be dehydrated and heated without any initial adjustment of the pH. In cases where the pH of the starch is more acidic, the pH is raised to a level effective to maintain the pH at neutral or greater during the subsequent dehydration and heating steps. At pH levels  
5 above 12, gelatinization more easily occurs, and the practitioner must take that into consideration in choosing processing parameters.

In practice, the pH is raised to neutral or greater, preferably to 7.5 to 12, and most preferably to greater than 8.0 to less than 10.5 before the dehydration and heating steps. While a pH higher than the  
10 preferred range may be used, such a pH will tend to increase browning of the starch during the heat treatment. However, the noncohesive textural and viscosity benefits of the heat treatment process tend to be enhanced as the pH is increased. In selecting the precise pH at which the starch will be heated, the practitioner will select a balance between  
15 color formation and functional characteristics.

In a preferred embodiment the native starch is slurried in water (e.g., 1.5 to 2.0 parts of water to 1.0 part of starch) or an aqueous medium and the pH is raised by the addition of any suitable base. After the pH of the starch has been brought into the desired pH range,  
20 the starch slurry is either dewatered and then dried, or dried directly. These drying procedures are to be distinguished from the dehydration step in which the moisture content is brought to 5% or below. In

another preferred pH adjustment step, a solution of a base may be sprayed onto the powdered starch. Buffers, such as sodium phosphate, may be used to maintain pH, if needed.

For food applications a food grade base is used. Suitable food  
5 grade bases for use in the pH adjustment step of the process include, but are not limited to, sodium hydroxide, sodium carbonate, tetrasodium pyrophosphate, ammonium orthophosphate, disodium orthophosphate, trisodium phosphate, calcium carbonate, calcium hydroxide, potassium carbonate, and potassium hydroxide, together  
10 with any other base approved for food use under Food and Drug Administration laws and other food regulatory laws. Bases not approved for food use under these regulations may also be used, provided they can be washed from the starch so that the final product conforms to good manufacturing practices (GMP) for food use. The  
15 preferred food grade base is sodium carbonate.

If the starch is not going to be used for a food use, the base need not be a food grade base, and any workable or suitable inorganic or organic base that can raise the pH of starch may be used.

It has been found that starch subjected to the heating step with  
20 a moisture content in excess of 15% results in a low viscosity product, and may result in a cohesive texture when dispersed in an aqueous medium and gelatinized. In a preferred embodiment, the starch is

dehydrated to a moisture content of 5% or less, more preferably 3% or less, and most preferably 1% or less, before the heating step. In the first stages of the heating, any residual moisture from the dehydration is quickly driven off, and heating occurs on the starch in an anhydrous state. Thus, as used herein, dehydration is intended to mean the removal of moisture from the starch, and heating is intended to mean heating an anhydrous starch. Both the dehydration and heating steps contribute to the formation of a starch product that has noncohesive texture and stable viscosity.

The dehydration can be accomplished in the same apparatus in which the heating step will occur, and most conveniently is continuous with the heating step. The dehydration and heating steps may be carried out in any apparatus fitted with a vent to the atmosphere such that moisture does not accumulate and precipitate onto the starch during the heating process. The apparatus is preferably equipped with a means for removing water vapor from the apparatus (e.g., a vacuum or a blower to sweep air from the head-space of the apparatus, fluidizing gas) during the heating step.

Any industrial oven including, but not limited to, conventional ovens, microwave ovens, dextrinizers, fluidized bed reactors and driers, mixers and blenders equipped with heating devices and other types of heaters, may be used in this step. Any combination of

processing conditions is suitable provided that the starch product has characteristics of a chemically crosslinked starch, including a short, smooth, heavy, noncohesive texture devoid of any sticky, cohesive aspects when dispersed and cooked in an aqueous medium at about  
5 0.1 to 35% solids.

The ideal time and temperature combination for the dehydration and heating steps will depend upon the equipment used, and may also be affected by the type of native starch being treated, the pH and moisture content of the starch, and other factors identified and selected  
10 by the practitioner. For example, when a conventional oven or batch dextrinizer is used, the dehydration step is carried out between 100°-140°C, and the heating step between 100°-200°C, preferably 120°C-180°C, more preferably 140° to 160°C, and most preferably about 160°C in order to obtain the heat treated starch product. At a  
15 temperature of 160°C, the heating step may be carried out for less than 5 hours. On an industrial scale, it may take 4 to 5 hours to equilibrate the starch temperature to 160°C prior to carrying out the heating step. Typically, shorter times will be required for higher temperatures and higher pHs.

20 When the heating apparatus is a fluidized bed reactor or drier, the dehydration step occurs simultaneously while bringing the equipment up to the final heating temperature. A similar temperature

profile may be used, but the product can be generated at a residence time of less than one hour at 160°C. It has also been discovered that the use of the fluidized bed provides superior starches having higher viscosities with less breakdown in viscosity, than could be achieved  
5 with other conventional heating apparatuses.

Following the heating step, the starch may be screened to select a desirable particle size, slurried in water and washed, filtered, and dried, bleached, or otherwise refined. The pH may be adjusted (e.g., to pH 4 to 6). The starch may be blended with other unmodified or  
10 modified starches, including pregelatinized starches, or with food ingredients before use in a food product.

The starches prepared by this heat treatment process can be used in food products that are manufactured with a heat processing step, such as, pasteurization or retorting. The starches also may be  
15 used in other types of food products where a non-chemically crosslinked, noncohesive starch thickener is required. Based on processed food formulations, the practitioner may readily select an amount of the starch product to provide the necessary viscosity and texture in the finished food product. However, the starch is preferably  
20 used at an amount of 0.1 to 35%, most preferably 2 to 6%, by weight, of the food product.

Among the food products that may be improved by the use of the starch product are baby foods, liquid infant formulations, heat treated and canned or jarred sauces and gravies, soups, salad dressings and mayonnaise, yoghurt, sour cream and other dairy products, pudding and pie fillings, liquid diet products and liquid products for hospital feeding. The starch products are also useful in dry mixes for sauces, puddings, baby foods, hot cereals, and the like, and are suitable for use in food applications where stability is required through all processing temperatures, including cooling, freezing and heating. For use in products subjected to temperature cycling operations, such as freeze-thaw cycling, a low temperature stable starch (e.g., waxy rice starch or flour or the "V.O." hybrid waxy maize starch of U.S. Patent number 4,428,972) is preferred.

The heat treated starches of this invention are also useful in non-food applications where chemically crosslinked starches are known to be useful.

Screening examples, and representative processes for making the heat treated starches and using them in foods are illustrated in the following examples.

20

#### **Screening Example 1**

This example screens various processing conditions for their effects on viscosity and texture of waxy maize, waxy barley, tapioca,

waxy rice, and V.O. hybrid starches. A sample of each granular starting starch was slurried in water, the pH of the slurry was adjusted with the addition of a 5% sodium carbonate solution, the slurry was agitated for 1 hour, then filtered and dried to less than 15% moisture content. The dry starch samples (150 g) were placed into an aluminum foil pan (4" x 5" x 1-1/2") in a conventional oven at 160°C to both dehydrate and heat the starch.

Brabender Evaluation of Waxy Maize. A sample of the heat treated waxy maize starch was slurried in water at neutral pH and 5.4% anhydrous solids, introduced to a Brabender Viscoamylograph for measurement of peak viscosity and breakdown, and heated rapidly to 50°C. The heat was increased by 1.5°C per minute to 95°C, and held for 20 minutes. The breakdown was measured as the difference between the peak viscosity and the viscosity after 20 minutes at 95°C. The samples were compared to a non-heat treated waxy maize control under the same Brabender evaluation conditions. The results given in Brabender Units (BU) are set out in Table I and show the production of an inhibited starch. This product is prepared by heat treating a 8.2 pH starch at 160°C for 4.5-5.5 hours.



**Table I**  
**Brabender Evaluation of Granular Waxy Maize Starch**

Sample	Process Variables			Brabender Viscosity	
	pH of the starch before heating	Heating Temp. (°C)	Time (Hours)	Peak Viscosity (B.U.)	Break-down at 95°C/20 Mins. (B.U.)
3	8.2	160	3.5	985	155
4	8.2	160	4.0	805	120
5	8.2	160	4.5	640	5
6	8.2	160	5.5	575	5
Control	naturally occurring (6.0)	none	none	1640	1010
1	(6.0)	160	2.0	1055	495
2	(6.0)	160	4.0	140	60

The remaining starches were screened subjectively for noncohesive properties and the results are set out in Table II. Waxy maize samples were gelatinized by slurring 7.0 g of starch (at 12% moisture) in 91 mls water at neutral pH and heating the starch slurry for 20 minutes in a boiling water bath. Barley, tapioca, rice and V.O. hybrid samples were gelatinized by slurring 7.5 g of starch (at 12% moisture) in 100 mls water at neutral pH and heating the starch slurry for 20 minutes in a boiling water bath. Evaluation was done by observation when the cooked starches cooled to room temperature. The results show that noncohesive properties can be obtained by heat

treating various starches at 160°C when the pH of the starch is not acidic.

**Table II**  
**Processing Variables and Evaluation for Noncohesiveness**  
**of Various Starches**

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Process Variables			
Sample	Heating (160°C)		Cold Evaluation of Gelatinized Samples at 25°C
	pH of the starch before heating	Time (hrs)	Texture
Waxy Maize <sup>a</sup>			
Control, unmodified <sup>b</sup>	naturally occurring	not heated	cohesive
Control, chemically crosslinked <sup>c</sup>	6.0	not heated	noncohesive
1	6.0	2	cohesive
2	6.0	4	(thin viscosity)
3	8.2	3.5	cohesive
4	8.2	4	slightly cohesive
5	8.2	4.5	noncohesive
6	8.2	5.5	noncohesive
7	8.2	6	noncohesive

	<b>Waxy Barley Starch<sup>d</sup></b>			
	<b>Control, unmodified</b>	<b>naturally occurring</b>	<b>0</b>	<b>cohesive</b>
5	1	8.7	1.5	cohesive
	2	8.7	2.5	slightly cohesive
	3	8.7	3.5	noncohesive
	4	5.2	1.5	(thin viscosity)
	5	5.2	2.5	(thin viscosity)
10	<b>Tapioca Starch<sup>e</sup></b>			
	<b>Control, unmodified</b>	<b>naturally occurring</b>	<b>0</b>	<b>cohesive</b>
	6	8.8	2	cohesive
15	7	8.8	3	cohesive
	8	8.8	4	slightly cohesive
	9	8.8	5	noncohesive
	10	5.5	3	(thin viscosity)
20	<b>Waxy Rice Starch<sup>f</sup></b>			
	<b>Control, unmodified</b>	<b>naturally occurring</b>	<b>0</b>	<b>cohesive</b>
	1	9.1	2	cohesive
	2	9.1	3	slightly cohesive
25	3	9.1	4	slightly cohesive
	4	9.1	5	noncohesive
	<b>V.O. Hybrid Starch<sup>g</sup></b>			
	<b>Control</b>	<b>5.9</b>	<b>0</b>	<b>cohesive</b>
30	1	8.7	2.0	cohesive

2	8.7	3.0	slightly cohesive
3	8.7	4.0	smooth cohesive
4	8.7	5.0	noncohesive
5	8.7	6.0	noncohesive

- 5 a. Waxy maize starch samples were commercial samples of granular waxy maize starch obtained from National Starch and Chemical Company, Bridgewater, New Jersey.
- 10 b. The unmodified waxy maize control was a commercial granular waxy maize starch obtained from National Starch and Chemical Company, Bridgewater, New Jersey.
- 15 c. The modified waxy maize control was a commercial crosslinked, (phosphorous oxychloride treated) granular waxy maize starch obtained from National Starch and Chemical Company, Bridgewater, New Jersey.
- 20 d. Waxy barley starch samples were commercial granular starch obtained from AlKo, Finland.
- 25 e. Tapioca starch samples were commercial granular starch obtained from National Starch and Chemical Company, Bridgewater, New Jersey.
- 30 f. Waxy rice starch samples were commercial granular starch obtained from Mitsubishi Corporation, Japan.
- g. V.O. hybrid starch samples were granular starches obtained from National Starch and Chemical Company, Bridgewater, New Jersey.

### Screening Example 2

This example illustrates the effect of starch moisture content during heating on the viscosity and texture of the treated starch.

Three samples of waxy maize starch from National Starch and  
5 Chemical Company, Bridgewater, New Jersey, (each 100 g) containing  
20.4% moisture were heated in an oven at 100°C in a sealed glass jar.  
Sample 1 was heated for 16 hours, sample 2 for 4 hours, and sample  
3 for 7 hours. The product viscosity and texture were subjectively  
compared to a 12.1% moisture granular waxy maize starch control by  
10 observation after the gelatinization procedure of Example 1. The  
starch samples had a pH of 5.2; no pH adjustment was made. None  
of the samples became noncohesive, and they remained as cohesive  
as the control starches that had not been heat treated.

### Screening Example 3

15 Samples of tapioca starch, waxy maize starch, and waxy rice  
flour were independently slurried in water, at 35% solids for the tapioca  
and waxy maize, and 30% solids for the waxy rice flour. The pH of  
each slurry was adjusted to between 9.4 to 9.6 with a 5% sodium  
carbonate solution. The pH adjusted slurry was then spray dried to 2-  
20 3% moisture.

A control sample for each of the starches was isolated from this batch and was not further dehydrated or heat treated.

Two samples, for each of the waxy maize and tapioca starches and the waxy rice flour, were separated from the spray dried material.

- 5 Each of these samples was dehydrated to less than 1% moisture at a temperature below 120°C, equilibrated to 160°C, and then heated at 160°C in a thermal reactor. The heating time for the samples ranged up to five hours.

- Brabender Evaluation Method. The control and samples were  
10 independently slurried at 5.0% anhydrous solids and adjusted to pH 3.0. Each slurry was introduced to a Brabender Viscoamylograph, heated rapidly to 92°C and held for 20 minutes. The same procedure was performed for the tapioca and waxy rice controls and samples, except that these were slurried at 6.3% solids. The viscosity was  
15 measured on a Brabender Viscoamylograph and breakdown was measured as the difference between the peak viscosity and the viscosity 10 minutes after peak viscosity. The results are given in Brabender Units (BU).

- Two viscosity and breakdown measurements were taken for the  
20 waxy maize starch and waxy rice flour samples, the second measurement following the first by approximately one hour. The tapioca samples were from two independent batches. The data are

recorded in Table III and show that heat treated starches are inhibited from breakdown of viscosity relative to native starches that were not heat treated. This inhibition correlated to a short, noncohesive texture in the cooled product.

5

Table III

Starch at pH 9.4-9.6 before heating		<u>Peak Viscosity</u> BU	<u>Breakdown</u> BU	
10	Tapioca	Control	1300	915
		Heat Treated	340	45
		Heat Treated	575	135
	Waxy Maize	Control	1135	730
		Heat Treated	640	25
		Heat Treated	580	20
	Waxy Rice Flour	Control	1140	833
		Heat Treated	695	10
		Heat Treated	600	10

**Example 4**

Samples of waxy maize starch and tapioca starch were heat  
 15 treated and evaluated for noncohesiveness. Two waxy maize samples  
 were prepared, one at an initial pH of 9.5 and the second at an initial  
 pH of 8.5. The tapioca sample was prepared at an initial pH of 9.5.

Each sample was heated from ambient temperature to within the range of about 155°-165°C and held for less than three hours in a conventional heating apparatus. Preparation of the pH adjusted starches was as follows:

5        A. Waxy Maize at pH 8.5. Waxy maize starch was slurried in water at 30-35% solids, and the pH of the slurry adjusted to 8.5 with a 5% solution of sodium carbonate. The slurry was filtered and flash dried to less than 8% moisture.

10       B. Waxy Maize at pH 9.5. Waxy maize starch was slurried in water at 30-35% solids, and the pH of the slurry adjusted to 9.5 with a 5% solution of sodium carbonate. The slurry was spray dried to less than 3% moisture.

15       C. Tapioca at pH 9.5. Tapioca starch was slurried in water at 30-35% solids, and the pH of the slurry adjusted to 9.5 with a 5% solution of sodium carbonate. The slurry was spray dried to less than 3% moisture.

20       D. Brabender Evaluation Method. A sample of each of the waxy maize starches slurried at 5.0% anhydrous solids and adjusted to pH 3.0 was introduced to a Brabender Viscoamylograph. The slurry was heated rapidly to 92°C and held for 20 minutes. The same procedure was performed for the tapioca sample, except that this was slurried at 6.3% solids. The viscosity breakdown measured as the



difference between the peak viscosity and the viscosity 10 minutes after peak viscosity were measured in Brabender Units on a Brabender Viscoamylograph. The data are recorded in Tables IV-VI and show that heat treated starches are inhibited from breakdown of viscosity relative to native starches that were not heat treated. This inhibition correlated to a short, noncohesive texture in the cooled product.

**Table IV**  
**Waxy Maize at 8.5 pH**

	<b>Heating Time Hours</b>	<b>Heating Temp. °C</b>	<b>Peak Viscosity BU</b>	<b>Breakdown BU</b>
10	12	163	560	70
	12.75	163	540	65
	11	162	530	75
15	10.25	168	530	70
	10.25	163	510	75

Heating Time = Time required to dehydrate and heat the starch from ambient temperature (this includes the holding time at the final temperature).

**Table V**  
**Waxy Maize at 9.5 pH**

	<b>Heating Time Hours</b>	<b>Heating Temp. °C</b>	<b>Peak Viscosity BU</b>	<b>Breakdown BU</b>
5	10.25	155	605	40
	11.0	162	530	30
	9.25	160	540	30
	10.0	162	470	55
10	9.5	166	440	25

Heating Time = Time required to dehydrate and heat the starch from ambient temperature (this includes the holding time at the final temperature).

**Table VI**  
**Tapioca at 9.5 pH**

	<b>Heating Time Hours</b>	<b>Heating Temp. °C</b>	<b>Peak Viscosity BU</b>	<b>Breakdown BU</b>
15	11.5	155	525	50
	9.0	165	500	35
20	6.0	158	905	305

Heating Time = Time required to dehydrate and heat the starch from ambient temperature (this includes the holding time at the final temperature).

### **Screening Example 5 Fluidized Bed Reactor**

Samples of waxy maize starch at naturally occurring pH (about 6.0) and adjusted with sodium carbonate to pH 8.5 and to pH 9.5 were prepared, dehydrated to less than 1% moisture, and then heated at 160°C in a fluidized bed reactor. The starch was simultaneously dehydrated and heated from ambient temperature to 160°C in less than three hours and then held at 160°C for the time showed in Table VII. Samples were evaluated for peak viscosity and inhibition to breakdown according to the Brabender evaluation method for the waxy maize samples in Example 4. The data are set out in Table VII and show that inhibited starches, with higher peak viscosities and less breakdown, can be obtained using the fluidized bed reactor compared to standard thermal reactors, and that these inhibited starches can be obtained at much shorter times than were possible with standard thermal reactors.

**Table VII**  
**Waxy Maize Heated at 160°C**

	<u>Initial</u> <u>pH</u>	<u>Heating Time</u> <u>min</u>	<u>Peak</u> <u>Viscosity</u> <u>BU</u>	<u>Breakdown</u> <u>BU</u>
5	6.0	0	1053	593
		30	710	250
		60	645	200
		90	570	130
		120	560	120
		150	485	90
	7.5	90	550	200
		120	470	145
		150	415	120
		180	380	100
	8.5	0	980	350
		30	770	115
		60	665	40
		90	625	25
		120	585	5
	9.5	0	1055	175
		30	825	25
		60	705	5
		90	690	0
		120	665	5

### Screening Example 6

This example shows the effects of the heating temperature and time on peak viscosity and inhibition for a waxy maize starch adjusted to pH 9.5 with a 5% solution of sodium carbonate. The peak viscosity  
5 and breakdown were measured on a Brabender Viscoamylograph according to the evaluation method of Example 4. The heating was done in a fluidized bed reactor similarly to Example 5. The samples were taken when the temperatures were achieved as shown in Table VIII. The results are set out in Table VIII and indicate that  
10 noncohesive samples can be obtained at heating temperatures between 100°C-200°C, with more inhibition obtained at higher temperatures or at longer times with lower temperatures.

**Table VIII**  
**Time and Temperature Study**

	<b>Heating Temp.</b>	<b>Time at Heating Temperature</b>	<b>Peak Viscosity (BU)</b>	<b>Breakdown</b>
5	110°C	22 hrs	1185	215
	160°C	0	1055	175
	160°C	120 min	665	5
	175°C	0	850	95
	180°C	0	715	35
10	190°C	0	555	5
	200°C	0	rising curve*	
	200°C	120 min	no viscosity	

\* Peak not reached

#### Food Example 7

15        This example illustrates the use of the starches in a processed food product, a retorted white sauce.

Part A: A white sauce was prepared from the formulation set forth below by (1) blending the dry ingredients and adding them to the milk and water with a no- shear Baldor Mixer (a Lightin' Mixer type unit); (2)  
20    heating the mixture to 80°C; (3) adding the liquid margarine and blending for 15 minutes; and (4) filling 10 ounce cans with the mixture and heat processing the canned sauce to an internal can temperature of 121°C (250°F) and a minimum Fo of 5 in a pilot scale, water immersion Stock 900 retort.

**White Sauce Formulation**

		<b>Ingredient</b>	<b>Percent by Weight</b>
5		Whole Milk	45.74
		Water	45.73
		Liquid Margarine	5.00
		Starch	2.20
		Salt	0.73
10		Wheat Flour	0.50
		White Pepper	0.05
		Nutmeg	0.05
		Total	100.00

The starches described in Table IX, below, were added to the white sauce and the sauces were tested prior to filling the cans and after retorting for viscosity (using a Brookfield RVT Viscometer with a #4 spindle at 10 rpm) and visually evaluated for texture and organoleptic quality. Results are shown in Table IX.

**Table IX**  
**Heat-Treated Waxy Rice Starch In Retorted White Sauce**

Starch <sup>a</sup>	Hot Fill Viscosity (cps)	Viscosity after Retorting (cps)	Description	Relative Rank <sup>b</sup>
1 <sup>c</sup>	200	1600	slightly thin, no lumps, slightly grainy	8.5
2 <sup>d</sup>	600	2800	smooth, no lumps, creamy	9.0
3 <sup>e</sup>	—	2000	slightly thin, a few lumps, slightly grainy	8.5
4 (control)	500	2400	very slightly grainy, slightly thin	8.0
cross-linked waxy <sup>f</sup> maize starch (control)	44	4400	grainy, thin, margarine separated <sup>f</sup>	7.0

- a. Samples 1-3 are heat treated waxy rice starches. Sample 4 is the un-processed rice starch base used in the preparation of Samples 1-3.
- b. Represents organoleptic ranking of 1-10 (10=best) for visual appearance and texture.
- c. Sample 1 was heated at 160°C for 0.5 hours at a pH=8.5 and a moisture content of 10.6%.
- d. Sample 2 was heated at 160°C for 1.0 hours at a pH=8.5 and a moisture content of 10.6%.
- e. Sample 3 was heated at 160°C for 2.0 hours at a pH=8.5 and a moisture content of 10.6%.



- 5 f. The initial heat treatment prior to filling the cans was insufficient to gelatinize the chemically crosslinked starch control. Therefore margarine separation was observed and the hot fill viscosity was quite low.

Although less viscous than chemically modified starches when used at the same percentage in the sauce formulation, the heat treated waxy rice starches thickened the sauce throughout processing, gave  
10 excellent texture, and were comparable in quality to, or better than, commercial starches used in retorted white sauces.

**Part B:**

A white sauce was prepared as described in Part A, except whole milk (91.47%) was used in place of the whole milk (45.74%) and  
15 water (45.73%) mixture used in Part A.

The waxy maize starches and control starches described in Table X, below, were tested in the white sauce by the methods of Part A. Results are shown in Table X.

**Table X**  
**Heat-Treated Waxy Maize Samples In Retorted White Sauce**

Starch Processing		White Sauce		
Sample	Heating Time (hours)	Viscosity After Retorting (cps)	Description	Relative Rank <sup>a</sup>
1 <sup>b</sup>	5.5	2825	tan, small lumps	8.0
2 <sup>b</sup>	4.5	4925	off-white, lumpy, creamy, slightly better than sample 1	8.0
3 <sup>b</sup>	4.0	6600	off-white, lumpy, thick, heavy	6.5
4 <sup>c</sup>	3.5	5200	some lumps, slightly cohesive	7.0
control-chemically cross-linked waxy maize starch <sup>d</sup>	—	4000	short, slightly grainy, slight margarine separation	7.5

- a. Represents organoleptic ranking of 1-10 (10=best) for visual appearance and texture.
- b. Samples 1-3 are waxy maize starch samples adjusted to a starting pH=8.5 with 5% Na<sub>2</sub>CO<sub>3</sub> solution and heated at 160°C for 4.0 to 5.5 hours.

- 5           c.    Sample 4 is the sample of waxy maize starch identified as Sample 3, Table I, Example 1, above.
- d.    Control starch was a commercial product obtained from National Starch and Chemical Company, Bridgewater, New Jersey.

          Although the results show a drop in viscosity in starch-thickened, retorted white sauce as the starch process is continued  
10   beyond 4.5 hours at a pH=8.5 for waxy maize starch, the relative ranking is acceptable. The starches were ranked as comparable to or better than the commercial, chemically crosslinked control in texture and organoleptic character.

#### **Food Example 8**

15           This example illustrates the use of heat treated waxy maize starch and waxy rice flour in a 25% fat salad dressing (mayonnaise type).

          The salad dressing was prepared by (1) blending the dry ingredients; (2) preparing a potassium sorbate solution; (3) adding the  
20   dry mixture to an aqueous phase containing the potassium sorbate solution and other aqueous liquids; (4) heating to 85°C for 5 min.; (5) cooling to 30°C; (6) adding an egg and oil mixture under vacuum and homogenizing the two mixtures; and (7) filling into glass containers.

**25% Fat Salad Dressing Formulation**

	Ingredient	% by Weight
	Water	42.58
	Sunflower oil	25.00
5	Fresh whole eggs	8.50
	Sugar	7.50
	Starch <sup>a</sup>	4.50
	Wine vinegar	3.50
	Tarragon vinegar	3.50
10	Mustard	2.20
	Salt	2.00
	Lemon vinegar	0.50
	Citric acid	0.20
	<u>Potassium sorbate</u>	<u>0.02</u>
15	Total	100.00

- a. The experimental starch and flour samples were adjusted for viscosity purposes to contain 5.00% starch. The control (a highly stabilized crosslinked chemically modified waxy maize starch) was used at 4.50% starch and the 0.5% difference was taken off the weight of the water.

Under relatively severe processing conditions (i.e., high shear) as well as the high acid (about pH 3.3) and fat content, both waxy maize starch and waxy rice flour gave excellent texture, creaminess, and homogeneity. In addition, the taste of the experimental products was comparable to that of the control. Although lower in viscosity compared to the control, the results of a short-term storage stability test revealed a stable product through at least 4 weeks of refrigerated storage. See Table XI, below for stability test results expressed as a

function of viscosity in cps units (Brookfield RVT Viscometer, #4 spindle, 10 rpm).

**Table XI**  
**Storage Stability of Salad Dressings**  
**Using Heat Treated Starch or Flour**

<b>Weeks of Refrigerated Storage</b>	<b>Control-Chemically Modified Starch</b>	<b>Heat-Treated Waxy Maize Starch</b>	<b>Heat-Treated Waxy Rice Flour</b>
	<b>cps</b>	<b>cps</b>	<b>cps</b>
0	21,500	13,500	10,250
1	17,250	12,250	8,500
2	17,000	11,750	8,250
3	18,000	11,500	9,000
4	17,250	11,500	9,250

#### **Food Example 9**

This example illustrates the use of the heat treated starches in baby food.

**Part A:** The heat treated starch is added to retorted plums using the following baby food formulation. The baby food is heated to 88°C (190°F), and held at 88°C for 10 minutes, placed in glass jars, sealed and retorted. The starch thickens the plums and gives them a noncohesive texture.

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**Plums-Baby Food Formulation**

	<b>Ingredient</b>	<b>Percent by Weight</b>
	Plums	23.00
	Sugar	15.00
5	Corn Syrup	15.00
	Starch	5.50
	<u>Water</u>	<u>51.50</u>
	Total	100.00

- 10 **Part B:** The heat treated starch is added to retorted cottage cheese using the following baby food formulation.

**Cottage Cheese Baby Food Formulation**

	<b>Ingredient</b>	<b>Percent by Weight</b>
	Cottage Cheese	35.0
15	<u>Water</u>	<u>13.0</u>
	Sugar	10.5
	Starch	4.5
	Pineapple Juice	4.0
	Reconstituted Lemon Juice	2.3
20	<u>Water</u>	<u>30.7</u>
	Total	100.0

- The cottage cheese and 13% of the water are thoroughly blended. A slurry of the remaining ingredients is prepared and cooked to 88 to 91°C (190 to 195°F). The cottage cheese and water are slowly added to the cooked mixture with agitation and the temperature is brought to 88°C (190°F). The hot product is placed in jars, sealed and retorted for 20 minutes at 116°C (240°F). The heat treated starch thickens the cottage cheese baby food and gives it a noncohesive texture.

**We Claim:**

1. A process for making a heat treated starch that is noncohesive when dispersed in an aqueous medium and gelatinized comprising the steps:
  - 5 a) providing a native granular starch at a neutral or basic pH;
  - b) dehydrating the starch to a moisture content of 5% or less; and
  - c) heating the dehydrated starch at a temperature of 100°C
- 10 or greater for a period of time effective to cause the starch to be noncohesive when it is dispersed in an aqueous medium and gelatinized, the heat treated starch being the functional equivalent to a chemically crosslinked or modified starch.
2. The process according to claim 1 in which the native granular
- 15 starch is selected from the group consisting of native granular corn, pea, potato, sweet potato, barley, wheat, rice, sago, amaranth, tapioca, sorghum, waxy maize, waxy rice, waxy barley, and combinations thereof.

3. The process according to claim 2 in which the starch is selected from the group consisting of potato, tapioca, waxy maize, waxy rice, waxy barley, and V.O. hybrid waxy maize starch.

4. The process according to claim 1 in which the starch is provided  
5 at a pH of 7.5 to 12.

5. The process according to claim 4 in which the starch is provided at a pH of greater than 8.0 to less than 10.5.

6. The process according to claim 1 in which the native starch is provided at a pH of neutral or greater by slurrying the starch in water  
10 and adding a sufficient amount of base to raise the pH of the starch to a level effective to maintain the pH at neutral or basic during the subsequent dehydration and heating steps.

7. The process according to claim 6 in which the base is selected from the group consisting of sodium hydroxide, sodium carbonate,  
15 tetrasodium pyrophosphate, ammonium orthophosphate, disodium orthophosphate, trisodium phosphate, calcium carbonate, calcium hydroxide, potassium carbonate, and potassium hydroxide.



8. The process according to claim 1 in which the native granular starch is dehydrated to a moisture content of 3% or less before the heating step.
9. The process according to claim 8 in which the native granular starch is dehydrated to a moisture content of 1% or less before the heating step.
10. The process according to claim 9 in which the native granular starch is dehydrated to anhydrous before the heating step.
11. The process according to claim 1 in which the starch is heated to a temperature within the range of 100°-200°C.
12. The process according to claim 11 in which the starch is heated to a temperature within the range of 120°-180°C.
13. The process according to claim 12 in which the starch is heated to a temperature within the range of 150°-170°C.
14. The process according to claim 1 in which the heating step is carried out in an apparatus equipped with at least one vent open to the atmosphere.

15. The process according to claim 1 in which the heating step is carried out in an apparatus equipped with a means for removing water vapor from the apparatus.
16. The process according to claim 15 in which the apparatus is a  
5 fluidized bed reactor.
17. The use of a fluidized bed reactor to prepare a heat treated starch that is noncohesive when dispersed in an aqueous solution and gelatinized using the process according to claim 1.
18. A heat treated starch prepared by the process according to  
10 claim 1.
19. A heat treated starch prepared by the process according to claim 1 having a Brabender viscosity of at least 140 B.U. in a 5.4% anhydrous solids dispersion at pH 3 after 20 minutes at 95°C.
20. A heat treated starch prepared by the process according to  
15 claim 1 that achieves no peak viscosity in a 5.4% anhydrous solids dispersion at pH 3 after 20 minutes at 95°C.

21. A heat treated starch prepared by the process according to claim 1 in which the native granular starch initially has been converted.
22. A heat treated starch prepared by the process according to claim 1 in which the native granular starch initially has been chemically  
5 modified to contain ether or ester substituents.
23. A food comprising at least one heat treated starch prepared by the process according to claim 1.
24. A food comprising 0.1 to 35% of at least one heat treated starch prepared by the process according to claim 1.
- 10 25. A starch heated to yield noncohesive texture when dispersed in an aqueous medium and gelatinized.
26. A process for making a heat treated flour that is noncohesive when dispersed in an aqueous medium and gelatinized comprising the steps:
- 15 a) providing a native granular flour at a neutral or basic pH;

b) dehydrating the flour to a moisture content of 5% or less;

and

c) heating the dehydrated flour at a temperature of 100°C or greater for a period of time effective to cause the flour to be  
5 noncohesive when it is dispersed in an aqueous medium and gelatinized, the heat treated flour being the functional equivalent to a chemically crosslinked or modified flour.

27. The process according to claim 25 in which the native granular flour is selected from the group consisting of native granular corn, pea,  
10 potato, sweet potato, barley, wheat, rice, sago, amaranth, tapioca, sorghum, waxy maize, waxy rice, waxy barley, and combinations thereof.

28. The process according to claim 27 in which the flour is selected from the group consisting of potato, tapioca, waxy maize, waxy rice,  
15 waxy barley, and V.O. hybrid waxy maize flour.

29. The process according to claim 25 in which the native flour is provided at a pH of 7.5 to 12.

30. The process according to claim 29 in which the native flour is provided at a pH greater than 8.0 to less than 10.5.
31. The process according to claim 25 in which the native flour is provided at a pH of neutral or greater by slurring the starch in water  
5 and adding a sufficient amount of base to raise the pH of the starch to a level effective to maintain the pH at neutral or basic during the subsequent dehydration and heating steps.
32. The process according to claim in which the base is selected from the group consisting of sodium hydroxide, sodium carbonate,  
10 tetrasodium pyrophosphate, ammonium orthophosphate, disodium orthophosphate, trisodium phosphate, calcium carbonate, calcium hydroxide, potassium carbonate, and potassium hydroxide.
33. The process according to claim 25 in which the native granular flour is dehydrated to a moisture content of 3% or less before the  
15 heating step.
34. The process according to claim 25 in which the native granular flour is dehydrated to a moisture content of 1% or less before the heating step.

35. The process according to claim 25 in which the native granular flour is dehydrated to anhydrous before the heating step.

36. The process according to claim 25 in which the flour is heated to a temperature within the range of 100°-200°C.

5 37. The process according to claim 11 in which the flour is heated to a temperature within the range of 120°-180°C.

38. The process according to claim 12 in which the flour is heated to a temperature within the range of 150°-170°C.

39. The process according to claim 25 in which the heating step is  
10 carried out in an apparatus equipped with at least one vent open to the atmosphere.

40. The process according to claim 25 in which the heating step is carried out in an apparatus equipped with a means for removing water vapor from the apparatus.

15 41. The process according to claim 15 in which the apparatus is a fluidized bed reactor.

42. The use of a fluidized bed reactor to prepare a heat treated flour that is noncohesive when dispersed in an aqueous solution and gelatinized using the process according to claim 25.

43. A heat treated flour prepared by the process according to claim  
5 25.

44. A heat treated flour prepared by the process according to claim 25 having a Brabender viscosity of at least 140 B.U. in a 5.4% anhydrous solids dispersion at pH 3 after 20 minutes at 95°C.

45. A heat treated flour prepared by the process according to claim  
10 25 that achieves no peak viscosity in a 5.4% anhydrous solids dispersion at pH 3 after 20 minutes at 95°C.

46. A heat treated flour prepared by the process according to claim 25 in which the native granular flour initially has been converted.

47. A heat treated flour prepared by the process according to claim  
15 25 in which the native granular flour initially has been chemically modified to contain ether or ester substituents.

48. A food comprising at least one heat treated flour prepared by the process according to claim 25.
49. A food comprising 0.1 to 35% of at least one heat treated flour prepared by the process according to claim 25.
- 5 50. A flour heated to yield noncohesive texture when dispersed in an aqueous medium and gelatinized.